Meeting today's emerging contaminants with tomorrow's research tools

TL Jones-Lepp

United States Environmental Protection Agency

Office of Research & Development

NERL-Environmental Sciences Division-Las Vegas Nevada USA

INTRODUCTION

Athens, GA

The United States Environmental Protection Agency is divided into ten Regions and twelve Program Offices.

The emerging contaminant research described in this presentation is an overview of research at EPA's Office of Research & Development's (ORD) four National Exposure Research Laboratories (NERL) located in: Athens, Georgia; Cincinnati, Ohio; Las Vegas, Nevada; and Research Triangle Park, North Carolina.

Cincinnati, OH

RTP, NC

Las Vegas, NV

INTRODUCTION

Under Section 304(a) of the Clean Water Act (CWA), EPA must develop and publish ambient water quality criteria.

Under Section 405(d) of the CWA, and pursuant to 40 CFR 503, EPA regulates the use and disposal of sewage sludge.

A proposed definition of *Emerging Contaminants*

Pollutants (biotic and abiotic) that are currently not included in routine monitoring programs and which may be candidates for future regulation, depending on research on their (eco)toxicity, potential health effects, public perception, and on monitoring data regarding their occurrence in the various environmental compartments. The Agency uses the term pollutant as defined in the CWA. Emerging pollutants are not necessarily new chemicals or known biologicals. They include pollutants that have often been present in the environment, but whose presence and significance are only now being elucidated (adapted from the EU NORMAN project: www.norman-network.com as of 9/13/2006).

What can we consider as “emerging contaminants”?

- As of April 2006, nearly 28 million organic and inorganic substances had been documented (indexed by the American Chemical Society's Chemical Abstracts Service in their CAS Registry; excluding bio-sequences such as proteins and nucleotides).

- Of these, fewer than a quarter million (240,000) were inventoried or regulated by numerous government bodies worldwide - - representing less than 2.5% of those that are commercially available or less than 0.9% of the known universe of chemicals.

Slide courtesy of Dr. Christian Daughton, USEPA

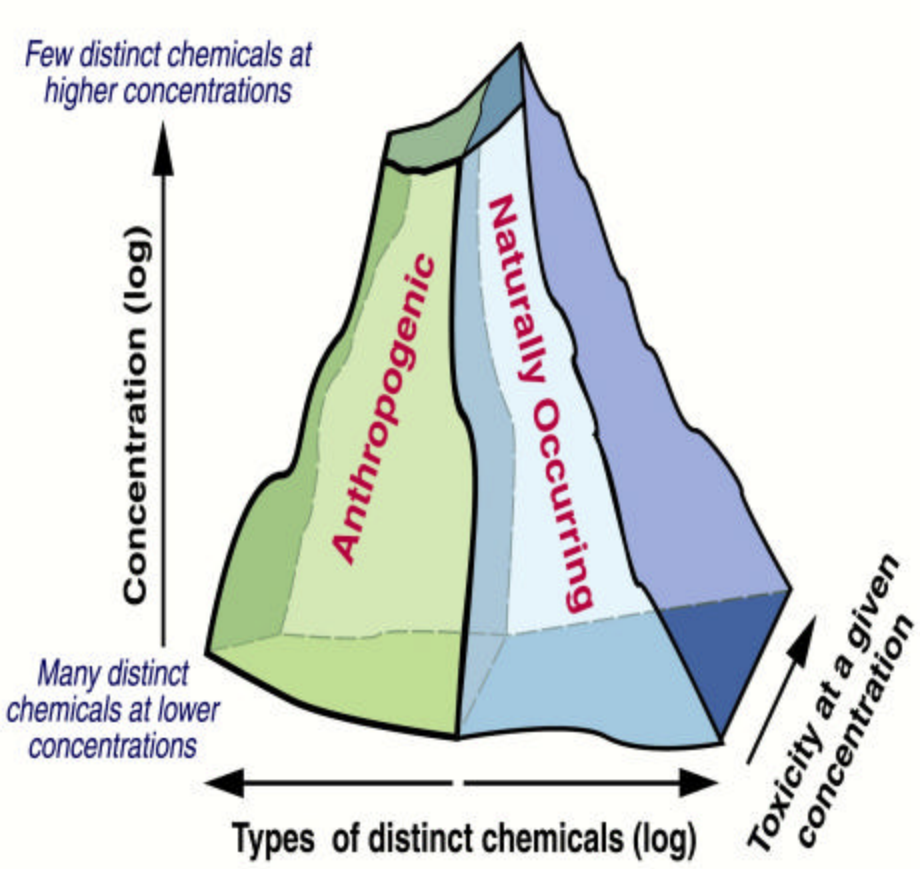
What can we consider as “emerging contaminants”?

- While the *KNOWN* universe of chemicals might seem large (28 million), the universe of *POTENTIAL* chemicals (those that could possibly be synthesized and those that already exist but which have not yet been identified) is unimaginably large.

- How many distinct organic chemical entities could hypothetically be synthesized and added to a seemingly limitless, ever-expanding chemical universe?

- By limiting synthesis strictly to combinations of 30 atoms of just C, N, O, or S, **more than 10^{60} structures are possible !**

- Expanding the allowable elements to other heteroatoms (e.g., P and halogens), the limits to the numbers of possible structures defies imagination. Also known as “chemical space”.



Slide courtesy of Dr. Christian Daughton, USEPA

Some examples of emerging contaminants

Anti-cancer drugs (e.g., tamoxifen, organoplatinum agents)

Bactericides (i.e., triclosan, triclocarban)

DBPs (Disinfection by-products) (e.g., iodo-acids, nitrosamines)

Fluorescent brighteners

Nanomaterials

- carbon-based, metal-heteroatom

Organotins

PBDEs (polybrominated diphenyl ethers)

Personal care products

- sunscreens, synthetic musks, NPEOs, etc.

PFOAs/PFOSs (perfluorinated organic acids)

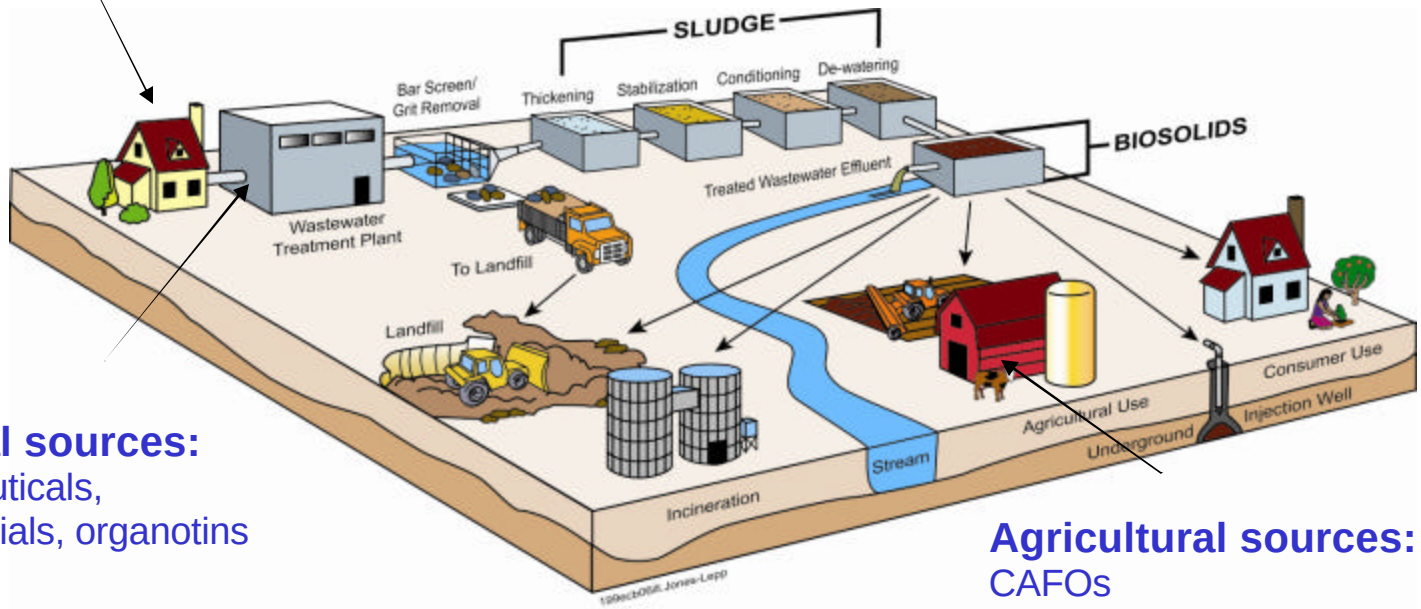
Pharmaceuticals

- diagnostic agents (e.g., X-ray contrast media), antibiotics, etc.

Prions

Possible sources of emerging contaminants

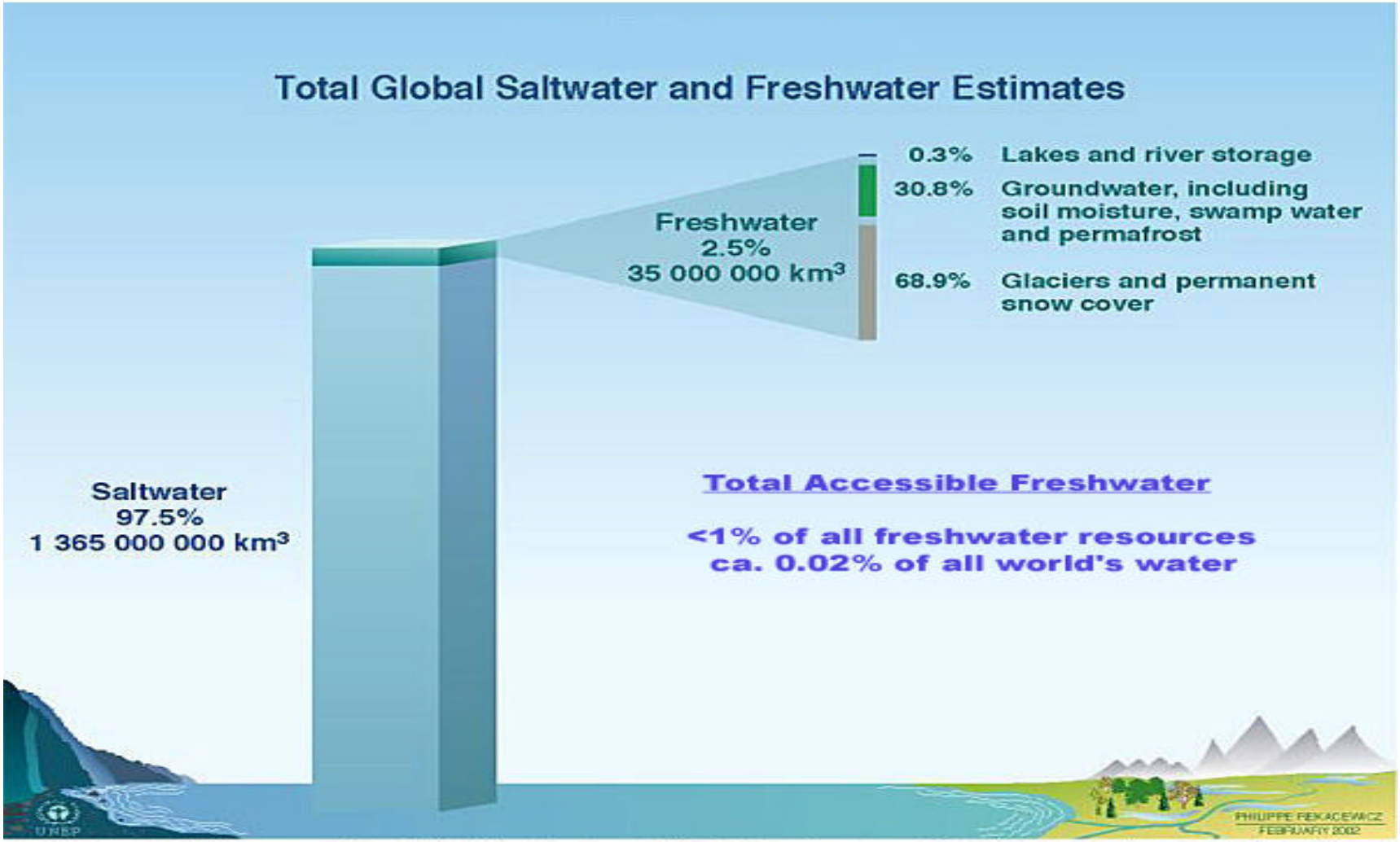
Consumers: Pharmaceuticals, nanomaterials in personal care products (e.g., sunscreens), personal care products (e.g., NPEOs, synthetic musks), detergents (fluorescent brighteners), PVC pipe (organotins)



Industrial sources: pharmaceuticals, nanomaterials, organotins

Agricultural sources: farming, CAFOs

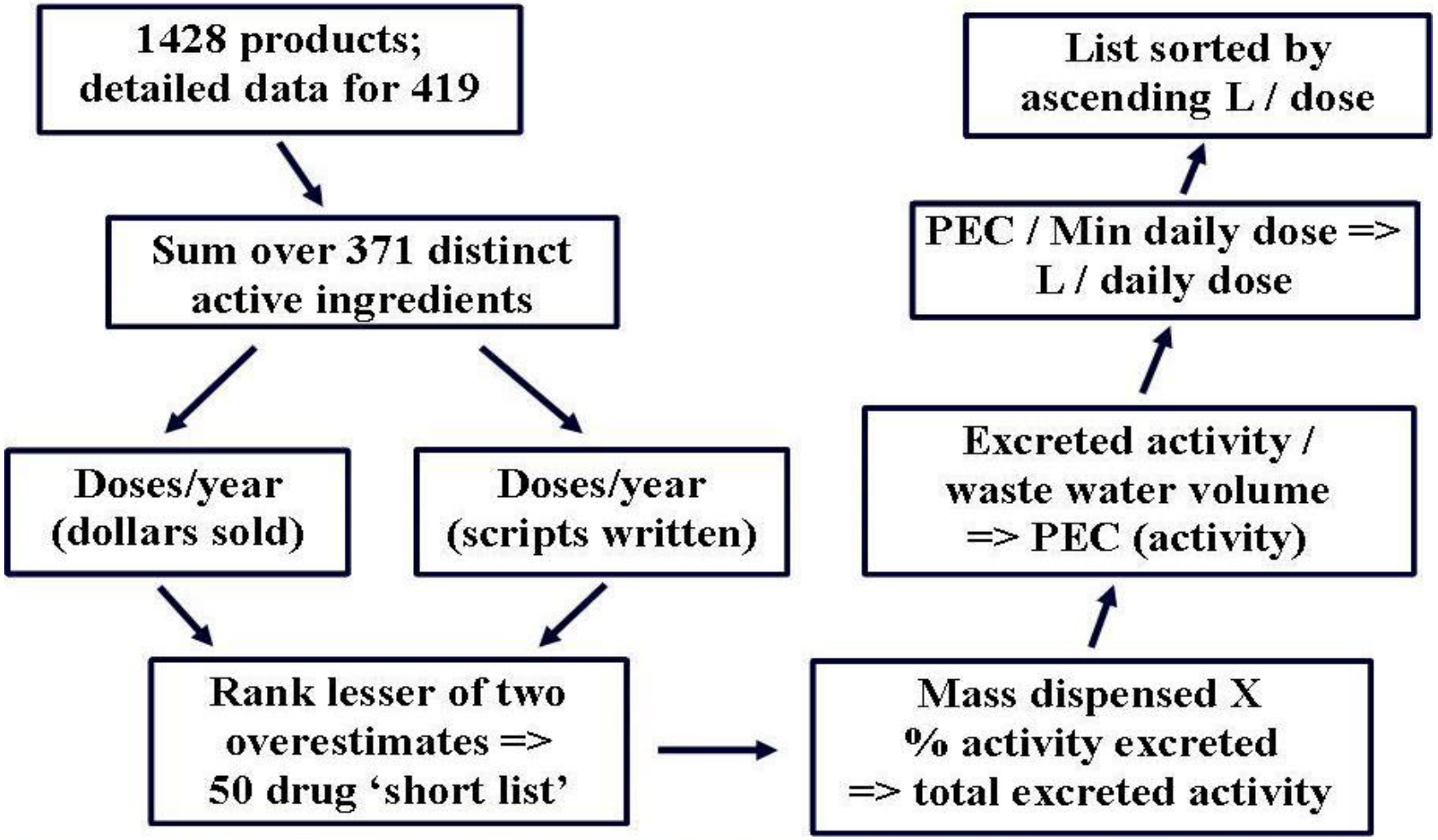
The World's Accessible Freshwater Resources



Source: Igor A. Shiklomanov, State Hydrological Institute (SHI, St. Petersburg) and United Nations Educational, Scientific and Cultural Organisation (UNESCO, Paris), 1999.

Source & Wastewater Emerging Contaminant Research

The model: data flow



Analytical Methods Development for 65 Ecologically Relevant Pharmaceuticals & Metabolites-Degradation Products

Angela Batt, Mitch Kostich, Dan Bender, USEPA, National Exposure Research Laboratory, Cincinnati, OH USA

Sample Collection

↓

Sample Preservation

↓

Dechlorination of Effluents

↓

Hydrolysis of any remaining conjugates?

↓

Solid Phase Extraction

↓

UPLC-MS/MS

Sample volume – 250 mL, 500 mL, or 1-L, add isotope surrogates, Filter

Preservation Options

Acid (pH 2) or alternative preservatives for labile compounds (sodium azide diazolidinyl urea or sodium pyrithione) to prevent microbial degradation

Ascorbic acid or ammonium chloride will be added to remove residual chlorine

Will investigate the effectiveness of enzyme hydrolysis (instead of acid)

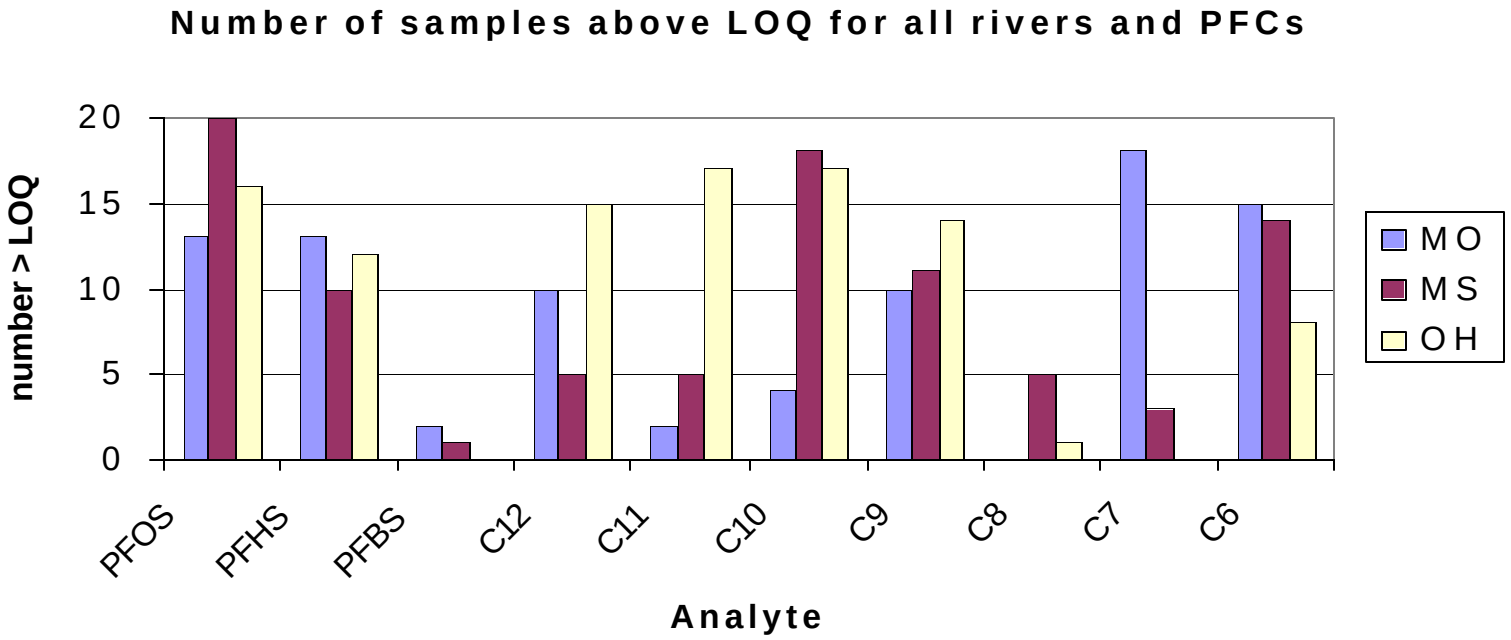
Extraction Options

Oasis HLB - reverse phase extraction cartridge
Oasis MCX - mixed mode sorbent with reverse phase and cation exchange capacities

Pilot Analyses Perfluorinated Compounds (PFOS, PFOA, PFHS, and other Perfluorinated Acids, C6-C12) in Fish Homogenates

Mark Strynar - NERL/HEASD

- Pilot Methods developed by Strynar/Lindstrom 2005 on existing 2004 homogenates.
- Analyze 10 Large and 10 Small Fish Samples from each river to determine whether analytical methods detect significant PFCs.



At each location, for each compound, the highest possible value is 20

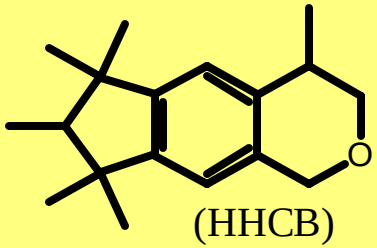
Synthetic Musk Research

Lantis Osemwengie, USEPA, ORD/NERL-ESD, Las Vegas, NV USA

Slide courtesy of Dr. Lantis Osemwengie

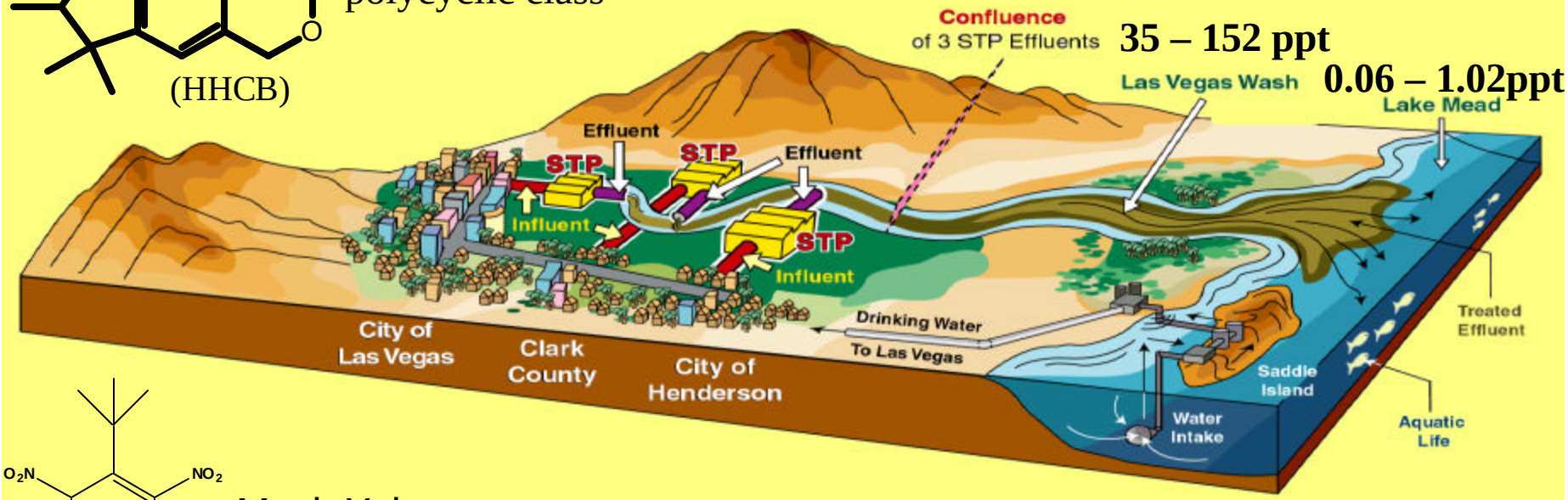
Origin, Transport & Fate of Synthetic Musk Compounds in the Las Vegas Basin

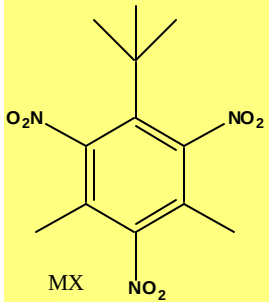
see Osemwengie et al.:
http://epa.gov/nerlesd1/chemistry/pharma/musks.htm



(HHCB)

Galaxolide:
polycyclic class





MX

Musk Xylene:
Nitro musk class

1400-4500 ppt

Slide courtesy of Dr. Lantis Osemwengie

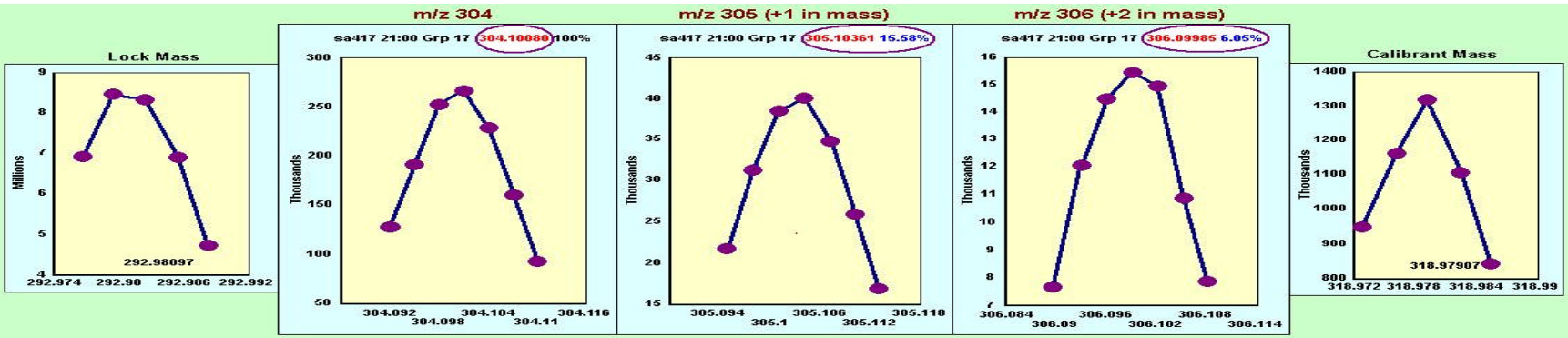
Identification of Compounds in South African Stream Samples Using High Resolution Mass Spectrometry with Ion Composition Elucidation Software,

Andrew H. Grange[1], Papo M. Thomas,[2] Mathebula Solomon[2], and G. Wayne Sovocool[1] [1]USEPA, NERL, Las Vegas, Nevada, USA, [2]Dept. of Water Affairs and Forestry, Institute for Water Quality, Pretoria, South Africa

INTRODUCTION Many target compounds have been identified and quantified in surface waters from industrialized countries. A major study by the USGS targeted 95 compounds in streams throughout the US. Analytical methods for target compounds usually employ clean-up procedures to remove potential mass interferences and utilize selected ion recording (SIR) to provide low detection limits. Such an approach, however, could overlook non-target compounds that might be present and that could pose risks to ecosystems or to humans. In an ideal world, all compounds present would be identified, quantified, and evaluated for toxicity.

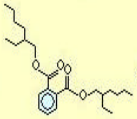
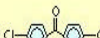
Ion Composition Elucidation (ICE) The US EPA's Environmental Chemistry Branch is identifying as many compounds as possible in combined acid and base/neutral extracts (1 mL total) of six 4-L stream samples collected near Johannesburg, South Africa, using Ion Composition Elucidation (ICE), a high resolution mass spectrometric technique developed in-house for a Finnigan MAT 900S double focusing mass spectrometer. This Selected Ion Recording (SIR) based technique measures the exact masses of an ion and its +1 and +2 isotopic mass peak profiles that arise from heavier isotopes such as 13C, 2H, 15N, 17O, 18O, 33S, and 34S. The abundances of the +1 and +2 profiles relative to the monoisotopic ion's profile are also measured for compounds by the technique illustrated below

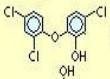
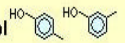
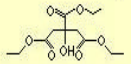
Partial Profiles Plotted from Selected-Ion-Recording Data



Slide courtesy of Dr. Andrew Grange

Table 1. Compound identities confirmed using standards

Compound	Structure	MS Match	Key Ion
acenaphthalene		★★	
anthracene		★★	$C_{10}H_{14}$
biphenyl		★★★	$C_{12}H_8$
fluoranthene		★★	
fluorene		★★	$C_{13}H_{10}$
1-methylnaphthalene		★	
2-methylnaphthalene		★	
naphthalene		★★★	
phenanthrene		★★	
dibutylphthalate		★★★★	
dimethylphthalate		★	$C_{10}H_{10}O_4$
diethylhexylphthalate		★★★★	$C_{16}H_{23}O_4$ (M-C_8H_{15})
4-chloro-3,5-dimethylphenol		★★★★	C_8H_9OCl
4,4-dichlorobenzophenone		★★★	$C_{13}H_8OCl_2$
1,2-dichlorobenzene		★★	$C_6H_4Cl_2$
1,3-dichlorobenzene		★	$C_6H_4Cl_2$
1,4-dichlorobenzene		★	$C_6H_4Cl_2$

Compound	Structure	MS Match	Key Ion
2,4-dichlorophenol		★	$C_6H_4OCl_2$
triclosan		★★	$C_{12}H_7O_2Cl_3$
2,6-dimethylphenol		★	$C_8H_{10}O$
2,3,6-trimethylphenol		★★	C_8H_9O (M-CH_3)
2,4-di-tert-butylphenol		★★★★	$C_{14}H_{22}O$
acetophenone		★★	C_8H_8O
benzophenone		★★	$C_{13}H_{10}O$
borneol		★★★	$C_{10}H_{18}O$
camphor		★★★★	$C_{10}H_{16}O$
cineole		★★	$C_{10}H_{18}O$
coumarin		★	
o-cresol		★★	
p-cresol and/or m-cresol		★★★	
p-cymene		★★	
dibenzofuran		★★★	$C_{12}H_8O$
dihydrocarvone		★★★★	$C_{10}H_{16}O$
2,3-dimethyl-2-cyclopenten-1-one		★	
ethylcitrate		★★	$C_{10}H_{13}O_5$
eugenol		★★★	$C_{10}H_{12}O_2$

Compound	Structure	MS Match	Key Ion
guaiacol		★	$C_7H_8O_2$
2,5-hexadione		★★	$C_6H_{10}O_2$
ibuprofen		★★★	$C_{13}H_{18}O_2$
menthol		★★★★	$C_{10}H_{18}$ (M-H_2O)
nonaldehyde		★★★★	
oxybenzone		★★	$C_{14}H_{12}O_3$
palmitic anhydride		★★★	
pentadecanoic acid		★★★★	$C_{15}H_{30}O_2$
1-tetradecene		★★	
1,2,4-trimethylbenzene		★	C_9H_{12}
1,2,3-trimethylbenzene		★	C_9H_{12}
tris(2-butoxy)phosphate		★★	$C_{12}H_{28}PO_6$ (M-$C_6H_{11}O$)
tris(2-chloroethyl)phosphate		★★★	$C_6H_{12}Cl_2PO_4$ (M-Cl)
atrazine		★★★★	
benzonitrile		★	
N-butylbenzenesulfonamide		★★★	$C_{10}H_{15}NO_2S$
caffeine		★★★	$C_8H_{10}N_4O_2$
carbamazepine		★★★★	$C_{15}H_{12}N_2O$

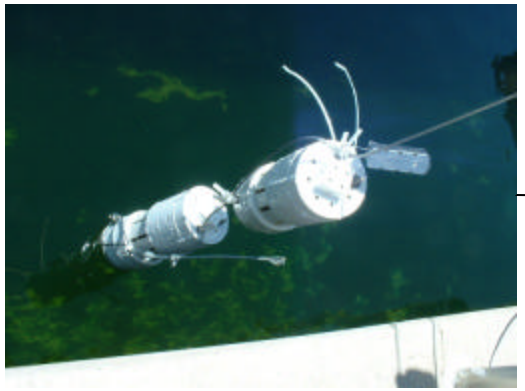
Compound	Structure	MS Match	Key Ion
1-cyanonaphthalene		★	$C_{11}H_7N$
N,N-diethyl-m-toluamide (DEET)		★★★★	$C_{12}H_{17}NO$
mesitylene		★★★	C_9H_{12}
methaqualone		★★	$C_{16}H_{14}N_2O$
2,6-dimethylquinoline		★★	$C_{11}H_{11}N$
3-ethenyl-4-methyl-1H-pyrrole-2,5-dione		★★	C_7H_7NO
2-phenylpyridine		★★	$C_{11}H_9N$
quinoline		★	C_9H_7N
terbuthylazine		★★★	$C_9H_{16}N_5Cl$
benzothiazole		★★★★	C_7H_5NS
2-(methylsulfonyl)-benzothiazole		Not in library	
2-(methylthio)-benzothiazole		★★★★	$C_8H_7NS_2$
skatole		★★	C_9H_9N
sulfur		★★	S_8
triphenylphosphate		★	

Slide courtesy of Dr. Andrew Grange

Advanced tools for assessing emerging contaminants in source waters and wastewater effluents

TL Jones-Lepp, USEPA, ORD/NERL-ESD, Las Vegas, Nevada USA
DA Alvarez, USGS, Columbia, Missouri USA

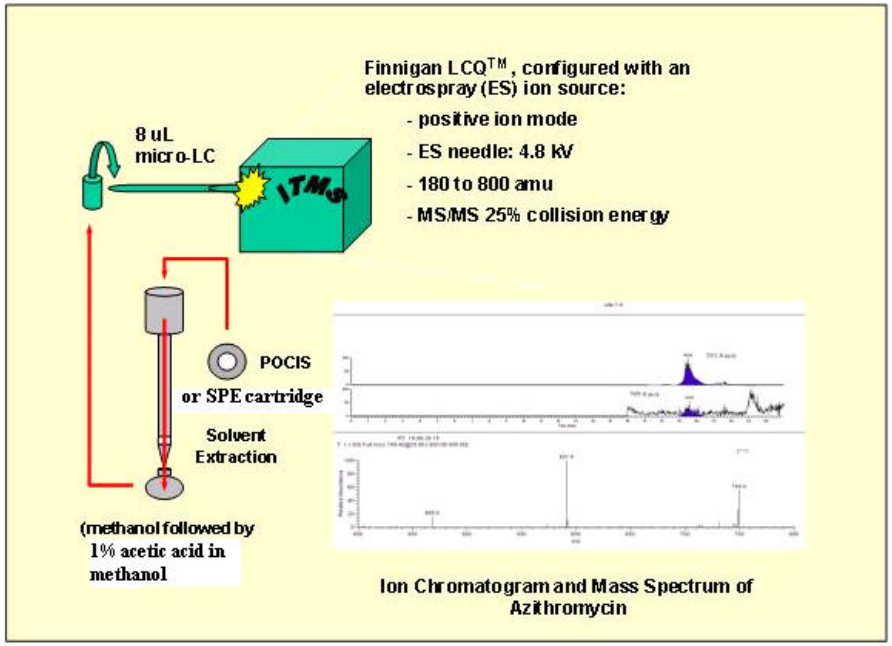
Field deployment



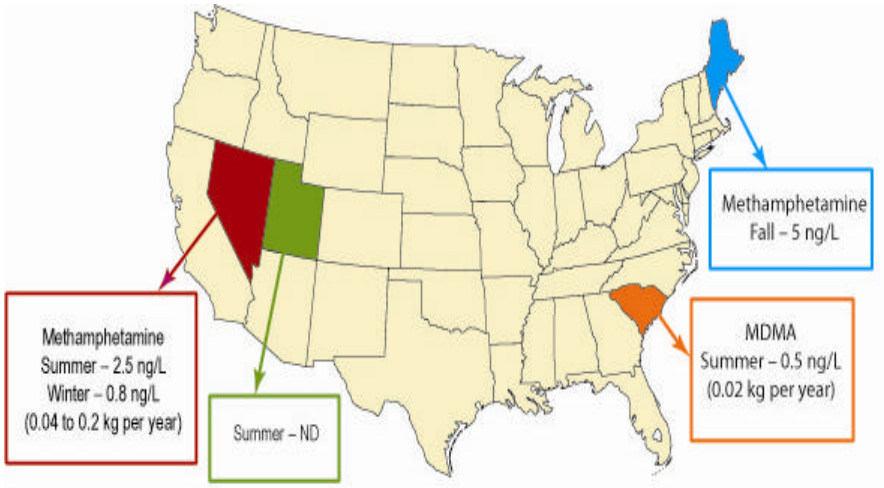
Polar Organic Chemical Integrative Sampler (POCIS)

Liquid chromatography-ion trap mass spectrometry

MS/MS for confirmation & quantitation



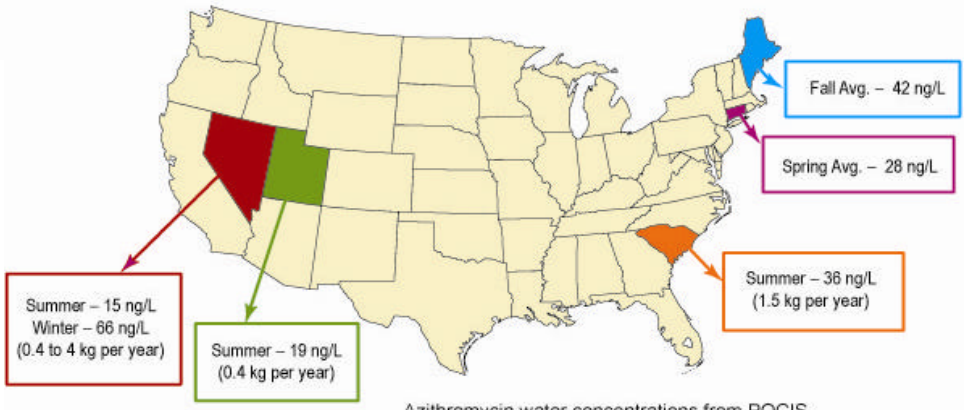
Results from monitoring emerging contaminants in source & wastewaters



Detection of methamphetamine and MDMA corresponds to regions of heightened drug usage according to the U.S. Drug Enforcement Agency.

Conclusions

- SPE HLB cartridges provide quick, accurate and convenient method for grab sampling.
- POCIS provides a time-weighted average concentration of sequestered, or related, chemicals which can be used for risk assessments
- U-LC-ESI/ITMS provides a quantitative and determinative method for accurate identification of unknown analytes.



Azithromycin water concentrations from POCIS and SPE extracts. Fluoxetine, levothyroxine, and omeprazole were not detected.

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Biosolids

Site(s)	Azithromycin ng/g dry wt	Clarithromycin ng/g dry wt	Roxithromycin ng/g dry wt
City of Milwaukee (Milorganite®)	14 (51)*	9 (18)	0.4 (2)
City of Los Angeles Hyperion WWTP*	25 (152)	20 (160)	nd
City of Las Vegas WWTP†	16	nd	nd

NA = not analyzed; ND = not detected ; *value in (-) reflects a “corrected” value based on % recoveries from each biosolids material.* Methamphetamine detected at 4 ng/g; †Methamphetamine detected at 5 ng/g.

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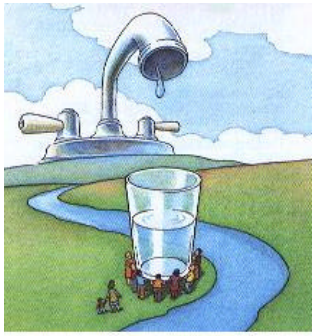
Drinking Water Emerging Contaminant Research

Persistence of Wastewater Compounds During Drinking Water Treatment: Removal and Potential Exposure

Susan Glassmeyer, USEPA, ORD/NERL-MCEARD, Cincinnati, Ohio
in collaboration with USGS, Denver, Colorado USA

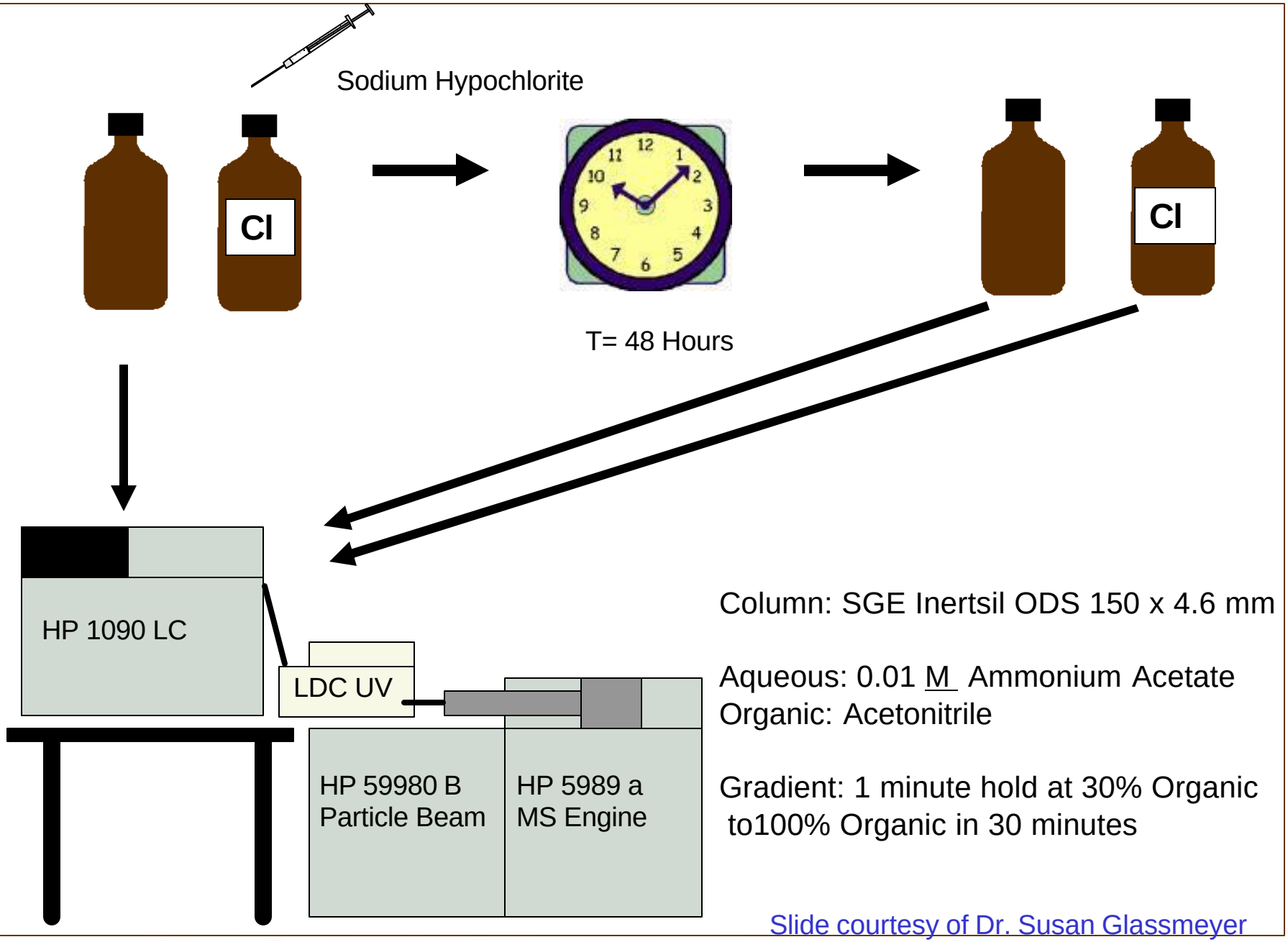


Objective: Examine drinking water facilities impacted by human wastewater (due to proximity to WWTP discharges, or reclaimed water facilities) to determine the "worst case scenario" of persistence of wastewater compounds (esp. pharmaceuticals) through drinking water treatment.

USGS will be developing two new methods. The first will incorporate pharmaceuticals not currently included in their methods; the second will focus on disinfection/ degradation by products of compounds known to be present in the raw/ source waters (FY 06)

Sampling will occur in two rounds. First Round: The raw and finished water of 10- 15 drinking water treatment facilities will be sampled to determine gross removal. Second Round: At least quarterly for one year, 2- 4 drinking water treatment facilities will be sampled throughout the treatment process to gauge the effectiveness of each step, and determine any effects of seasonality on the compounds found in the water (FY 07- 09)

Slide courtesy of Dr. Susan Glassmeyer



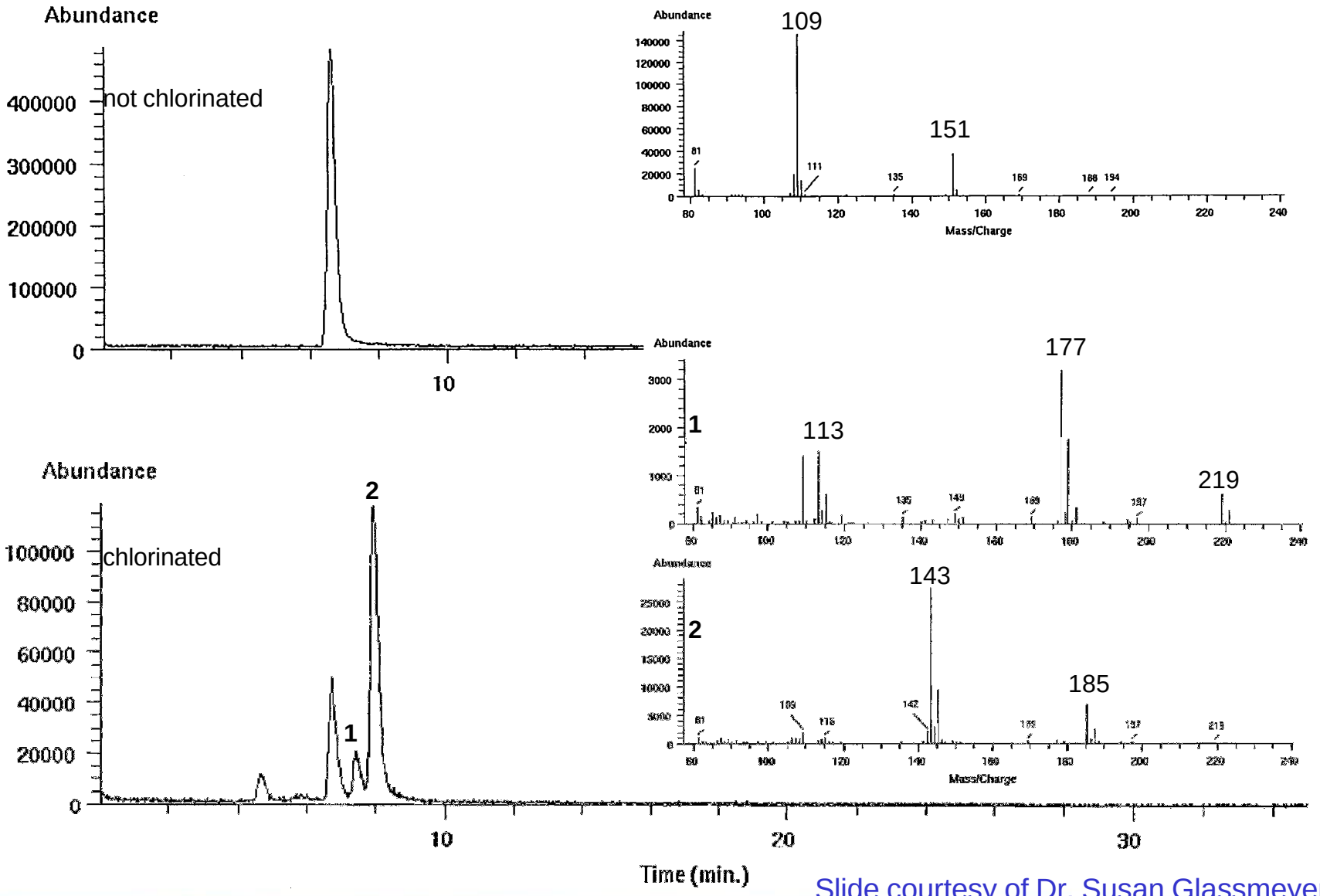
Column: SGE Inertsil ODS 150 x 4.6 mm

Aqueous: 0.01 M Ammonium Acetate
Organic: Acetonitrile

Gradient: 1 minute hold at 30% Organic
to100% Organic in 30 minutes

Slide courtesy of Dr. Susan Glassmeyer

Acetaminophen (MW = 151.17)



Slide courtesy of Dr. Susan Glassmeyer

Lessons Learned

- Disinfection is one route for the removal of pharmaceuticals from water
- The addition of chlorine to the molecule is not common (at least not as seen by particle beam)
- Ramification on environmental occurrence?
- Glassmeyer, S.T.; Shoemaker, J.A. Effects of Chlorination on the Persistence of Pharmaceuticals in the Environment Bulletin of Environmental Contamination and Toxicology. 2005, 74, 24-31.
- Bedner, M.; Maccrehan, W. A. Transformation of acetaminophen by chlorination produces the toxicants 1,4-benzoquinone and N-acetyl-p-benzoquinone imine Environmental Science & Technology 2006, 40, 516-522.

Slide courtesy of Dr. Susan Glassmeyer

Drinking Water Disinfection Byproducts (DBPs)

Susan Richardson, U.S. EPA, ORD/NERL- ERD, Athens, Georgia USA

Emerging DBPs

Halonitromethanes

Iodo-THMs

Iodo-acids

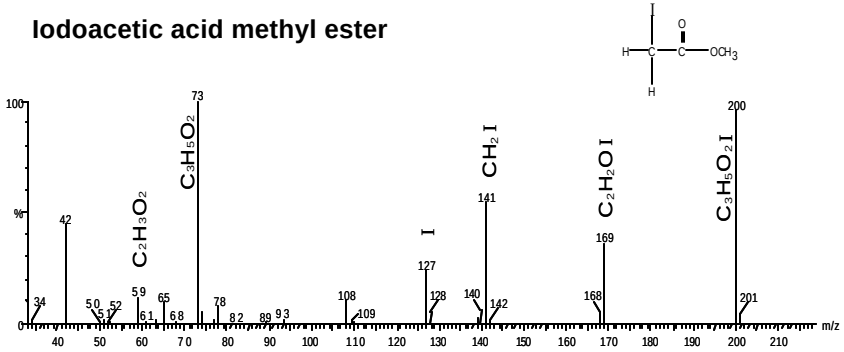
Haloamides

- Formed by the reaction of disinfectants with natural organic matter
- Concern over possible human health risk:
- Epi studies: risk of bladder cancer; some cause cancer in laboratory animals
- Recent concerns about possible reproductive & developmental effects (from epi studies)

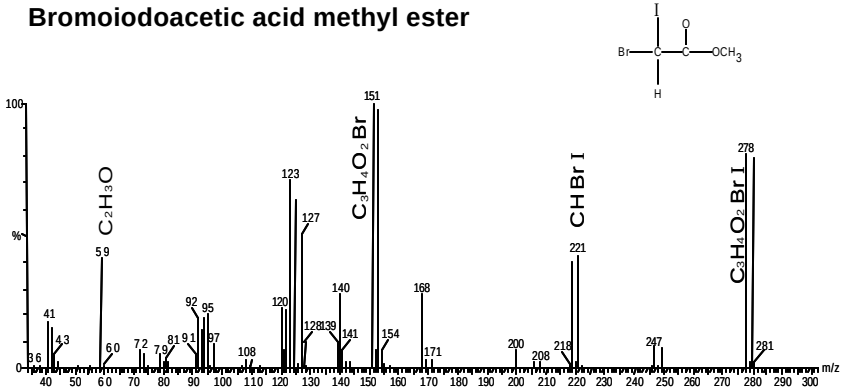
- Identified using GC/EI-MS
- Formed at levels comparable to regulated DBPs
- Increased formation with alternative disinfectants (ozone, chloramines)
- More genotoxic and cytotoxic than regulated DBPs

EI Mass Spectra of Iodo-Acids

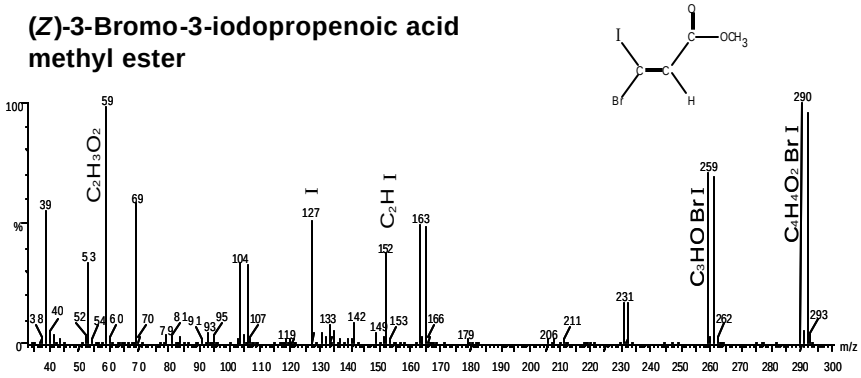
Iodoacetic acid methyl ester



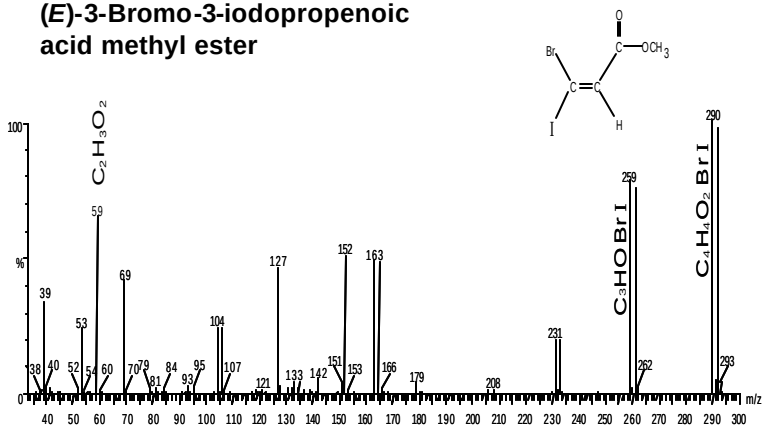
Bromoiodoacetic acid methyl ester



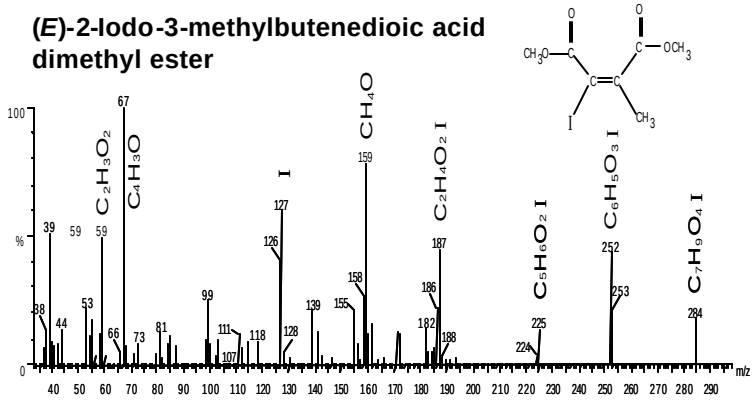
(*Z*)-3-Bromo-3-iodopropenoic acid methyl ester



(*E*)-3-Bromo-3-iodopropenoic acid methyl ester



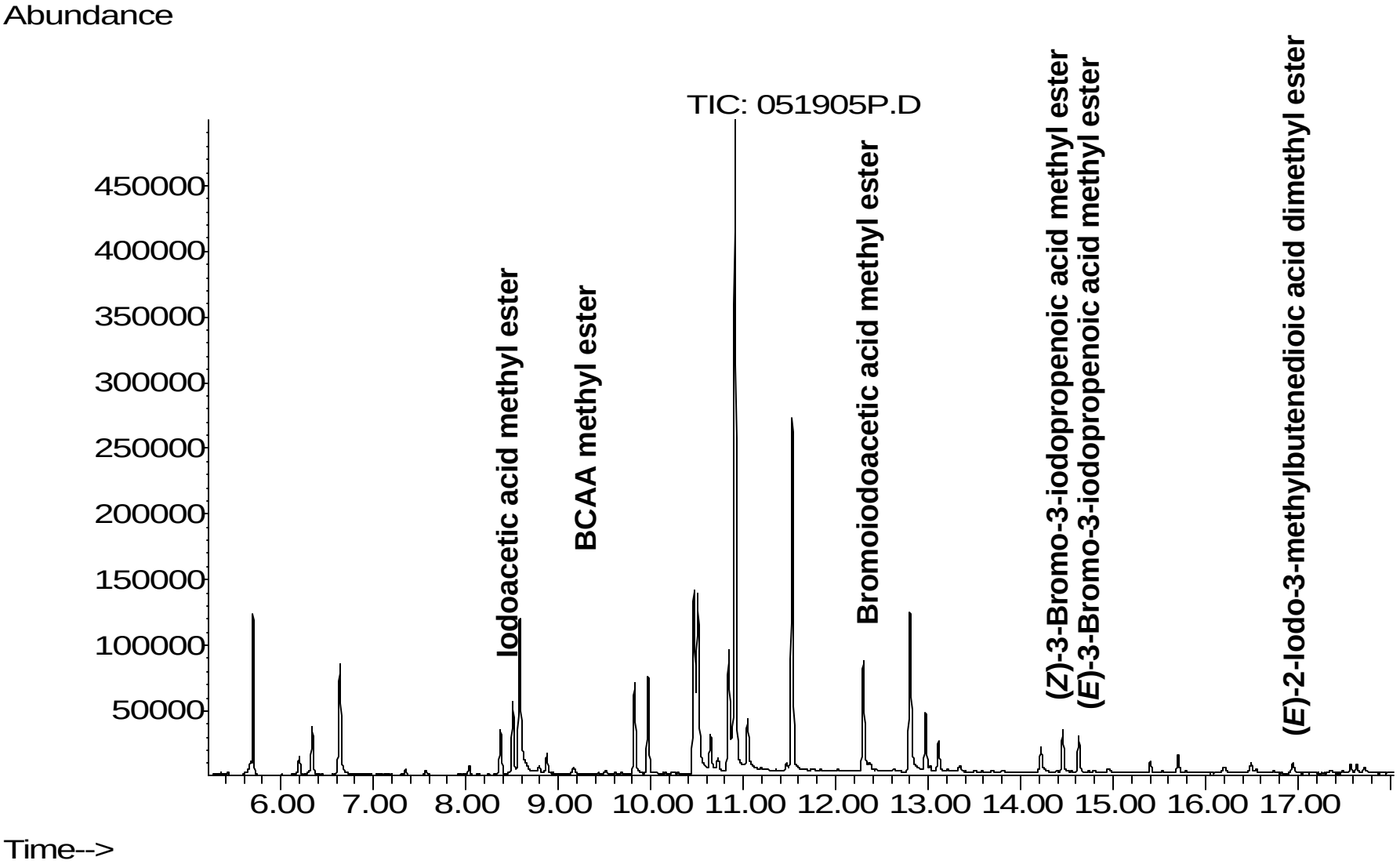
(*E*)-2-Iodo-3-methylbutenedioic acid dimethyl ester



GC/EI-MS (with high resolution) originally used to identify iodo-acids

Slide courtesy of Dr. Susan Richardson

Example of One Plant Sampled (SIM of m/z 127)



Slide courtesy of Dr. Susan Richardson

METHOD DEVELOPMENT FOR CCL AND EMERGING CONTAMINANTS IN DRINKING WATER USING GAS CHROMATOGRAPHY/MASS SPECTROMETRY

Jean W. Munch and Margarita V. Bassett, USEPA, ORD/NERL-MCEARD, Cincinnati, OH USA

NDMA and other Nitrosamines

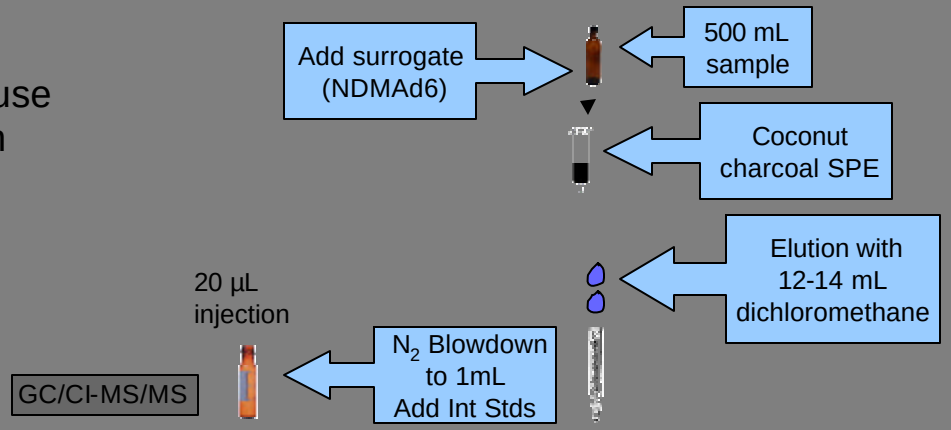
Environmental Issue

Emerging contaminants

- Occur in the environment as byproducts of manufacturing processes
- NDMA is especially associated with the manufacture of rocket fuel
- NDMA is also a drinking water disinfection byproduct
- Miscible with water and highly mobile in ground water
- Identified in treated wastewater, causing concern in areas of water re-use
- Highly carcinogenic - one in a million lifetime cancer risk at low ng/L concentrations

Approach

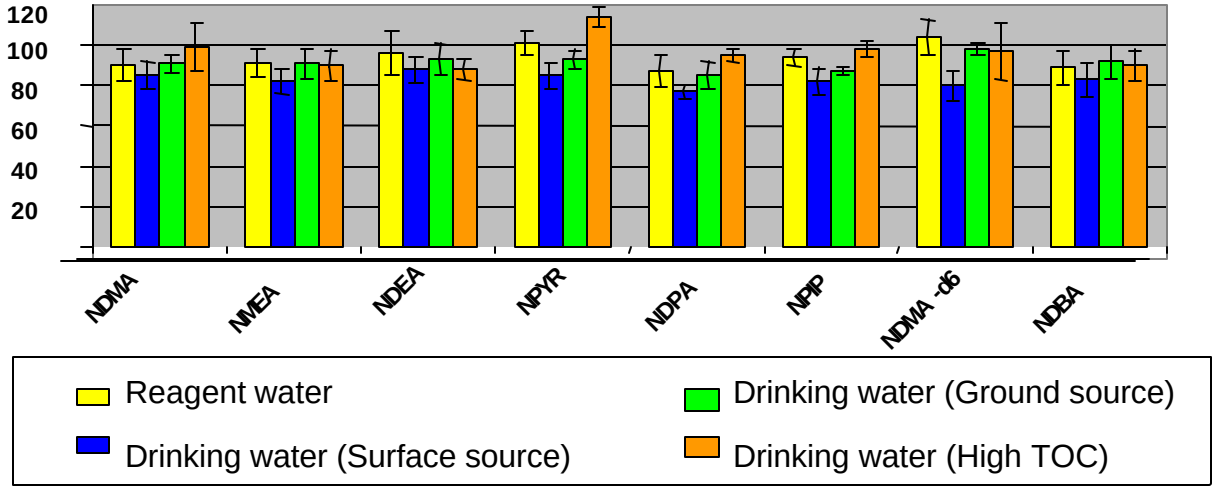
- Sensitivity ? Efficient extraction from water using carbon based SPE
  - ? Chemical ionization MS
  - ? Large volume injection GC
- Specificity ? MS/MS
- QC ? Use deuterated nitrosamines as surrogate and internal standards



Results

Lowest Concentration Minimum Reporting Level (LCMRL) range 1.2 -2.1 ng/L

Precision and Accuracy Data for Nitrosamines in Multiple Water Matrices
Fortified conc. 20 ng/L, N=6 for each matrix



Conclusions

SPE on coconut charcoal is an effective way to extract and concentrate nitrosamines from drinking water. When this extraction procedure is combined with the analysis of extracts by GC/CI-MS/MS, the result is a method that is sensitive, specific, accurate and precise.

This work resulted in the publication of USEPA Method 521.

courtesy of Jean Munch

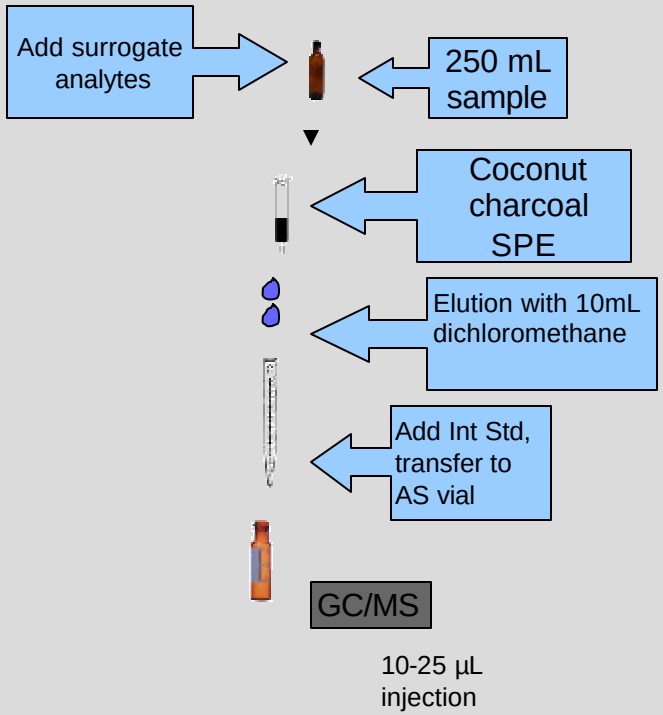
Jean W. Munch and Margarita V. Bassett, USEPA, ORD/NERL-MCEARD, Cincinnati, OH USA

1,4 Dioxane and other Water Soluble Volatiles

Environmental Issue

- Emerging contaminants that include: Solvents, solvent stabilizers, fuel additives and their degradations products
- Water solubility makes these contaminants highly mobile in ground water
- 1,4-Dioxane has been used in large amounts as a stabilizer for degreasing solvents, which historically were discarded by land application
- 1,4-Dioxane has a one in a million lifetime cancer risk of 0.003 mg/L
- t-Butanol (TBA) is a metabolite of the fuel additive methyl-t-butyl ether

Approach



- Sensitivity

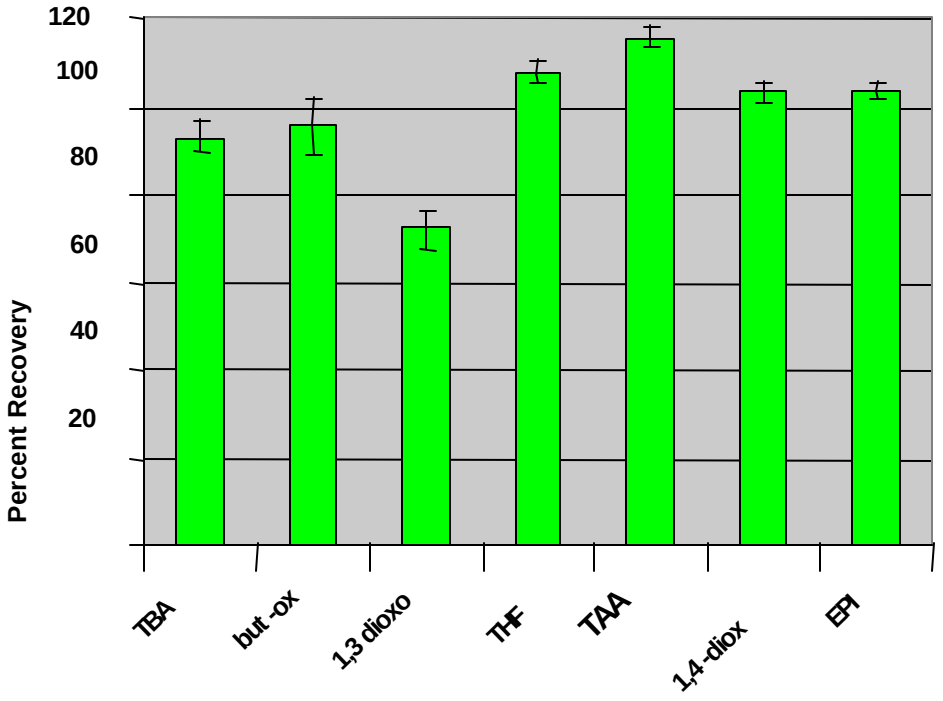
? Efficient extraction using coconut charcoal SPE

- QC ? Use of deuterated internal standards and surrogates
- Specificity ? GC/MS

? Large volume injection GC/MS

Results

Analyte Recovery - 250 mL Fortified Reagent Water (4 µg/L) Extracted on 2g Coconut Charcoal, Eluted with 10 mL DCM, 20 uL injection, N=4



Conclusions

SPE on coconut charcoal shows promise as a potential technique for extraction and concentration of water soluble volatile compounds. Combined with large volume injection GC/MS, low µg/L reporting limits can likely be achieved.

courtesy of Jean Munch

Acknowledgments

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